

T-1

Mechanics of Materials & Equation-of-State

Crystal Structural Stability of Actinide Elements from Electronic Structure Theory

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The structural properties of the elemental actinides, like many of the properties of actinide materials, are interesting and unusual. The equilibrium volumes of the early actinides (Th \rightarrow Pu) decrease parabolically with $5f$ occupation, as transition metals do as a function of d -band filling. There is a large increase in volume from plutonium to americium, and the post-Pu actinides show only a slight contraction with increasing $5f$ occupation, similar to the lanthanide contraction in the rare earth elements. This similarity between post-Pu actinides and the rare earths is exhibited also in equilibrium crystal structures. In contrast, the early actinides (apart from thorium) crystallize in open, low-symmetry structures, quite unlike transition metal structures. The ground state crystal structures of neptunium (simple orthorhombic with eight atoms per cell) and plutonium (simple monoclinic with sixteen atoms per cell, Figure 1) are unique in the periodic table. The high-temperature structures of the light actinides are equally interesting. A charge density wave forms in uranium between 20 and 50 K, and both neptunium and plutonium undergo several structural phase transitions with increasing temperature. The structural properties of plutonium are of particular interest. The low-temperature phase (α -Pu, mentioned above) is unique in the periodic table. This phase has the largest thermal expansion coefficient of all metallic elements. In contrast, the most useful plutonium phase (δ -Pu), stable between 592 and 724 K apparently has the simplest crystal structure (face-centered-cubic with one atom per cell), a volume 25% expanded over α -Pu, and a negative thermal expansion coefficient. Alloying with small amounts of Al or Ga stabilizes this phase to low temperatures. The measured elastic constants of this phase exhibit the largest anisotropy of any cubic element.

The basic structural properties of the actinides have been investigated for the past eighteen years by *ab-initio* electronic structure calculations using the Local Density

Approximation to the electron exchange/correlation functional [1-8]. These calculations have done much to illuminate the physical mechanisms underlying the structural properties of the actinides, but it has been only recently that these calculations have been accurate enough to give precise, quantitative theoretical information on structural properties [4-8]. This accuracy has been difficult

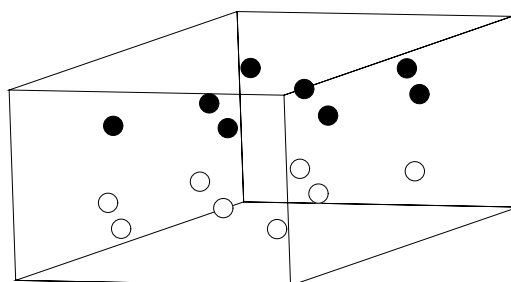


Figure 1: The unit cell of α -Pu.

to achieve because of the open, complex structures involved, the importance of relativity, and the number of electronic states involved in actinide bonding. Also important has been the utilization of an exchange/correlation functional that accounts for the large electron density gradients present in the actinides [5]. The principal computational tool that has been used to achieve this accuracy is an electronic structure

method developed in T-1. Virtually all accurate *ab-initio* calculations of actinide structural properties that have been performed have used this method.

The trend in the equilibrium volumes of the actinides is consistent with bonding $5f$ electrons from Th \rightarrow Pu and nonbonding $5f$ electrons from Am on. This picture is supported quantitatively by the electronic structure calculations described above. The agreement between calculated volumes and experimentally measured low-temperature volumes is consistent with the accuracy achieved in the rest of the periodic table. Calculations performed for Am with $5f$ electrons forced to be nonbonding reproduce the Am volume and crystal structure sequence under pressure with good accuracy [8]. In addition, calculations performed for the actinides Th \rightarrow Pu give the correct ground state structure for all these elements as well as correct crystal structural sequences with pressure. Another feature that is reproduced by *ab-initio* calculations is the increase in volume from Np to Pu. The source of this upturn has been debated until very recently. The present

calculations [6] show that this increase is a result of the less homogenous structure favored for α -Pu. A principle result of these recent *ab-initio* studies has been to show that the tendency toward low-symmetry structures in the light actinides in general (and the unique structure of α -Pu in

tetragonal (Bain) shear. Alternatively, if the $5f$ states are localized in this metal, one would expect them to give rise to magnetic order, as observed in the trans-plutonium metals. However, experiments show that δ -Pu is a Pauli paramagnet down to the lowest studied temperature, 50 K. The

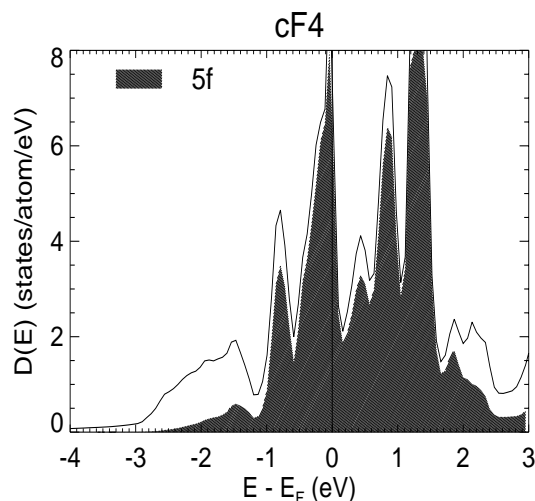


Figure 2: The calculated density of states of fcc-Pu.

particular) is the result of normal metallic bonding, arising from $5f$ electrons, in a regime of narrow bandwidths [7]. Symmetric structures and narrow, partially occupied $5f$ bands inevitably lead to a high density of states at the Fermi energy (Figure 2, fcc-Pu), and any symmetry-breaking distortion that moves weight away from the Fermi energy (Figure 3, α -Pu) will have an appreciable effect on the total energy, overcoming the cost in electrostatic energy on going to open structures if the bandwidth is small enough. In fact, all light actinides which have an appreciable occupation of itinerant $5f$ states display low-symmetry structures arising from this mechanism. With this understanding, the zero temperature structural properties of the actinides Th \rightarrow Pu are quantitatively described by itinerant, bonding $5f$ electrons. Past Pu, the actinide series suffers a Mott transition, and the actinides from Am onward are well described by localized, nonbonding $5f$ electrons.

This inclusion of the α phase of Pu in a unified description of the light actinides strengthens, by contrast, our ignorance of the true nature of the δ phase of Pu, which would be represented by Figure 2 in the calculations described. The properties of this allotrope do not fit our understanding of either the $5f$ -bonded light actinides or the localized $5f$ -trans-Pu actinides. Its structure is simple (fcc, giving the DOS in Figure 2); if the $5f$ states are situated in the vicinity of E_F , one may ask why the structure does not distort to lower its symmetry. Theoretical calculations treating the $5f$ s as itinerant give a minimum energy close to the α volume, and predict the fcc structure in Pu to be unstable against a

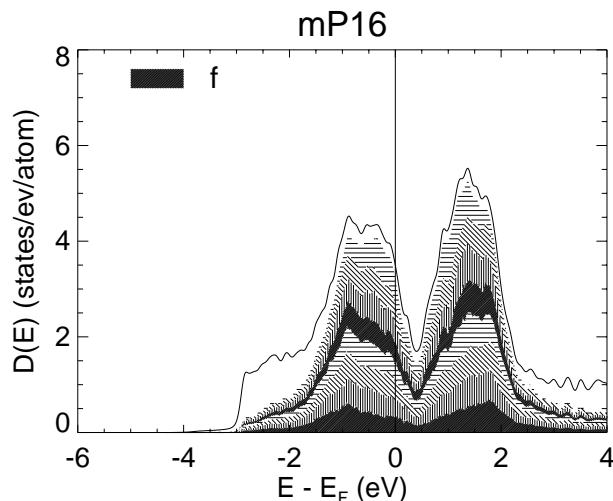


Figure 3: The calculated density of states of α -Pu.

equilibrium volume is also hard to reconcile with either delocalized or localized $5f$ states. The equilibrium volume of δ -Pu is $\sim 25 \text{ \AA}^3$ and is thus midway between the α -Pu ($\sim 20 \text{ \AA}^3$)—which has bonding $5f$ states, and α -Am ($\sim 29 \text{ \AA}^3$)—which has localized $5f$ states. Hence experimental and theoretical data available indicate that δ -Pu cannot be categorized in either of the two actinide subgroups, and that there is still much to learn about the basic microscopic, electronic properties of this unique material.

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